

## INFLUENCE OF COAL RANK ON OIL YIELD IN LOW-SEVERITY HYDROPYROLYSIS WITH AND WITHOUT A DISPERSED CATALYST

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### ABSTRACT

Although hydropyrolysis processes have been historically associated with high yields of methane and light hydrocarbon gases, oil yield and selectivity can be optimised by operating at relatively low temperatures ( $< 550^{\circ}\text{C}$ ) and moderate pressures ( $\sim 150$  bar). Indeed, when a dispersed catalyst such as sulphided molybdenum is employed in fixed-bed hydropyrolysis, liquid yields are comparable to those achieved in direct liquefaction. The influence of coal rank on oil yields with and without the Mo catalyst has been investigated using some of the Argonne coals, a number of European bituminous coals and Turkish lignites and an Australian brown coal. Without catalyst, oil yields broadly increase with decreasing rank and total conversions correlate reasonably well with volatile matter content. In catalytic hydropyrolysis, total conversions approach the reactive maceral contents for the bituminous coals investigated containing 80–83% dmmf C. For the lower-rank coals, the improvements in oil yields upon catalyst addition are much more variable, which probably reflects the differing degrees of success in limiting retrogressive char-forming reactions.

### INTRODUCTION

Our recent studies have shown that tar yields in excess of 60% daf coal can be achieved in fixed-bed hydropyrolysis for bituminous coals using dispersed sulphided molybdenum (Mo) catalysts<sup>(1,2)</sup>. Relatively low temperatures (500–520°C) have been employed to maximise the selectivity to tar (% tar/% hydrocarbon gases  $> 5$ ) whilst a hydrogen pressure of 150 bar has been sufficient to achieve maximum conversion. Although dispersed Mo catalysts have been widely used for batchwise hydrogenation<sup>(3,4)</sup> and direct liquefaction<sup>(5-7)</sup>, the early use of these catalysts in hydropyrolysis failed to achieve a high selectivity to liquid products<sup>(8,9)</sup> because of the high temperatures and pressures employed.

The experimental work to date<sup>(1,2,10,11)</sup> has mostly been conducted using a typical UK bituminous coal (Linby, 82% dmmf C). In this study, the influence of coal rank on conversions and tar composition in fixed-bed hydropyrolysis has been investigated using a selection of US and European coals, together with an Australian brown coal and immature kerogen samples.

### EXPERIMENTAL

#### Samples

Proximate, elemental and maceral analyses for the suite of coals and kerogens investigated are listed in Table 1. The suite includes 4 European

bituminous coals, 3 Turkish lignites, an Illinois No. 6 coal, two of the Argonne premium coal samples, an Australian brown coal and immature Type I (Goynuk) and II (Messel) kerogens. Only the N. Dakota lignite and Wyodak sub-bituminous coal could be used from the Argonne premium coal sample bank as the free swelling indices (FSI) of the bituminous coals were too high (FSI > 4) and gave rise to blockages in the reactor. The Illinois No. 6 sample (Herrin) used here had a FSI of 2.5 compared to a value of 4 for its Argonne counterpart.

For one of the European bituminous coals (Point of Ayr), samples of clarain and durain were also used having the following maceral composition

	% v/v	
	Clarain	Durain
Exinite	4	27
Vitrinite	93	30
Inertinite	2	42

For catalytic tests, the coals were loaded with 1% Mo from an aqueous solution of ammonium dioxodithiomolybdate which decomposes upon thermolysis to yield sulphided Mo<sup>(11)</sup>.

#### Hydropyrolysis

The fixed-bed hydropyrolysis reactor and experimental procedure has been described previously<sup>(2,11)</sup> the following conditions being used here.

Temperature	:	520°C
Pressure	:	150 bar
Heating rate	:	5°C s <sup>-1</sup>
Hold time	:	10 min
Volumetric flow rate	:	10 dm <sup>3</sup> min <sup>-1</sup>
Wt of coal	:	5 g mixed with 10 g sand

Char yields were determined from the weight loss of the reactor tube and tar yields from the weight gain of the dry-ice cooled trap (only a small amount of water - typically less than 1% daf coal - was condensed in the trap). Gas was recovered, sampled and analysed for C<sub>1</sub>-C<sub>4</sub> hydrocarbon gases. Tars were recovered in dichloromethane for characterisation by NMR, size exclusion chromatography, NMR and other appropriate techniques.

## **RESULTS AND DISCUSSION**

### Yields and tar composition

Tables 2 and 3 list the tar, char and gas yields obtained with and without the Mo catalyst for the suite of coals and kerogens and Figure 1 compares the tar yields. Without the catalyst, tar yields and total conversions (100%-char) broadly increase with decreasing rank. Indeed, total conversions correlate reasonably well with the volatile matter contents of the coals (Figure 2). It is noteworthy that tar yields of > 50% daf coal were achieved without catalyst for the immature kerogens and some of the low rank coals.

As reported previously for Linby coal<sup>(1,2)</sup>, the Mo catalyst gives rise to

marked increases in tar yield for bituminous coals (Figure 1) without concomitant increases in hydrocarbon gas yield with the highest yield of over 70% daf coal being achieved for the Herrin coal. Indeed, for Linby, Gedling and the Herrin coals, the total conversions are similar to their reactive maceral contents (exinite + vitrinite, Tables 1 and 2). However, for the two higher rank bituminous coals (Westerholt and Pt. of Ayr, 84 and 87% dmmf C, respectively), tar yields are lower and the total conversions are somewhat less than their reactive maceral contents. Thus, the available evidence suggests the highest tar yields in catalytic hydropyrolysis for bituminous coals are achieved for those containing ~ 80-83% dmmf C with inertinite concentrations below 20%.

The bulk compositions of all the tars from the bituminous coals are broadly similar, typical analytical data being summarised in Table 4. Catalytic hydropyrolysis tar generally have lower oxygen and sulphur contents and slightly higher number average molecular weights (as determined by SEC) than their non-catalysed counterparts.

Since total conversions are considerably higher for lower rank coals in non-catalytic hydropyrolysis (Table 2), the potential for improving tar yield with catalysts is much less than for bituminous coals. However, for the low rank coals and kerogens investigated, the effect of the Mo catalyst on conversions is extremely variable with increases in tar yield of between 5 and 20% daf coal being obtained (Table 3 and Figure 1). For the Turkish and N. Dakota lignites and Wyodak sub-bituminous coal, increases in tar yield were below 10% compared to over 15% for the Australian brown coal. Indeed, the char yields of over 25% for the lignites and Wyodak sub-bituminous coal are higher than those for the low-rank bituminous coals (80-83% dmmf C). Reasons for the differing behaviour of bituminous coals and most of the low rank coals investigated are discussed below.

#### Hydropyrolysis vs. batchwise hydrogenation

It is informative to compare coal rank trends in hydropyrolysis and batchwise hydrogenation with and without the sulphided Mo catalyst. For a small suite of coals, it was reported previously that at 400°C and 70 bar pressure (cold), measured by chloroform-solubles were higher for bituminous coals (80-85% dmmf C) than for a sub-bituminous coal and lignite<sup>(12)</sup>. However, with the Mo catalyst, oil yields increased with decreasing rank and reducing the temperature from 400 to 350°C accentuated the rank effect due to the greater number of labile heteroatomic bonds in lower rank coals. Thus, the trends in batchwise hydropyrolysis with and without catalyst are diametrically opposed to those in low-severity hydropyrolysis reported above.

These different rank trends are thought to arise from the relatively slow heating rate in batchwise hydrogenation and long residence time at 350-400°C where the Mo catalyst is most effective for promoting hydrogenolysis and heteroatomic bond cleavage reactions and minimising retrogressive reactions. In contrast, the heating time through this critical temperature window in the hydropyrolysis regime used here is only 10 s and, particularly for the more reactive lower rank coals, this may not be sufficient to prevent char forming retrogressive reactions. In addition, the bitumen generated during the early stages of reaction (pyrobitumen) remains in the reactor during hydrogenation while it can obviously volatilise to tar during hydropyrolysis. Because the bitumen generated from low rank coals is generally more paraffinic and volatile

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in nature than that from bituminous coals, it is probably less effective for mediating hydrogen atom transfer to initiate bond cleavage reactions.

#### Maceral concentrates

The results for the maceral concentrates from Pt. of Ayr coal (Table 5) support the assertion that the bitumen generated during catalytic hydrolysis plays a key role in tar generation. For the durain sample containing 27% v/v exinite, the total conversion of ~ 60% daf coal is close to the reactive maceral content. In contrast, the conversion for the clarain sample containing 2% exinite is much less than that anticipated from that for the whole coal (Table 3). Clearly, exinite has a synergistic effect on vitrinite conversion probably due to the high concentration of pyrobitumen generated in pyrolysis. Experiments on low temperature solvent extracted coals are in progress to gain further insight into the role of pyrobitumen.

#### ACKNOWLEDGEMENTS

The authors thank the EC for financial support (Grant No. EN3V-0048-UK (H)) and Mr. B. J. Stokes and Mr. G. Kimber of British Coal Corporation and Dr. W. Wanzl of Bergbau Forschung for supplying the UK bituminous coals, the maceral concentrates and the Westerholt coal respectively..

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Table 1. Analyses of Coals and Kerogens

Sample No.	Bituminous Coals			Argonne Coals		
	Pt. of Ayr	Westerholt	Linby	Cedling	Illinois No. 6	Wyodak sub-bit. lignite
	1	2	3	4	5	6
Volatiles matter % daf	36.3	40.6	37.9	39.2	47.4	49.0
C	87.2	84.0	83.0	81.6	80.7	76.0
H	5.8	5.8	5.5	5.2	5.2	5.4
O	4.4	8.4	9.4	9.4	10.1	16.9
N	1.6	1.6	1.9	1.7	1.4	1.1
Total	1.7	1.1	1.9	1.0	4.8	0.6
% d.b. S						
Pyritic	1.0	-	0.8	0.1	2.8	0.2
Exinite	14	-	10	8	5	<1
Vitrinite	66	-	74	72	85	89
Inertinite	19	-	16	20	10	11
a - mineral matter/shale free basis						
Turkish lignites						
Kerogens						
Australian brown coal						
Loy Yang						
Sample No.	8	9	10	11	12	13
Volatiles matter % daf	55.0	48.4	56.1	45.7	90.9	80.5
C	65.3	65.9	62.9	68.8	73.9	71.4
H	6.2	5.4	6.5	5.7	8.2	9.2
Ob	24.2	20.0	21.8	26.2	N.D.	N.D.
N	2.2	1.5	2.1	0.5	N.D.	1.6
% d.b. S						
Total	1.4	6.1	1.6	0.4	2.9	3.5
Pyritic	0.4	0.6	N.D.	N.D.	N.D.	1.3
b - by difference						
N.D. = not determined						

Table 2 Hydropyrolysis yields without the Mo catalyst

Coal	No.	Conversion	Char	Tar	C <sub>1</sub> -C <sub>4</sub> gases
Pt. of Ayr	1	46	54	38	7
Westerholt	2	51	49	38	4
Linby	3	52	48	38	7
Gedling	4	45	55	34	6
Illinois	5	55	45	46	N.D.
Wyodak	6	58	42	47	"
Nth Dakota	7	67	33	52	"
Coynuk	8	70	30	47	"
Can	9	68	32	48	"
Seyitomer	10	75	25	55	"
Loy Yang	11	66	34	49	3
Messel kerogen	12	85	15	65	5
Coynuk Shale	13	73	27	56	4

Table 3 Hydropyrolysis yields with the Mo Catalyst

Coal	No.	Conversion	Char	Tar	C <sub>1</sub> -C <sub>4</sub> gases
Pt. of Ayr	1	61	39	48	11
Westerholt	2	73	27	61	8
Linby	3	79	21	52	10
Gedling	4	71	29	64	10
Illinois	5	84	16	75	9
Wyodak	6	73	27	56	N.D.
Nth Dakota	7	70	30	61	"
Coynuk	5	77	23	56	10
Can	3	74	26	52	6
Seyitomer	10	81	19	60	10
Loy Yang	11	86	14	65	5
Messel Kerogen	12	89	11	84	6
Coynuk Shale	12	98	2	90	2

Table 4 Bulk properties of hydropyrolysis tar from bituminous coals

C	84 - 87
H	6.8 - 7.5
% O	3 - 6*
N	1.5
S	0.5 - 1.0*
M <sub>n</sub>	250 - 280
Aromatic H, mole %	30 - 35
% Asphaltenes	25 - 40

\*For a given coal, % O and S lower for tar obtained with catalyst

Table 3 Hydrocracking yields from several concentrations of Point  
Ave. coal

Coal	Catalyst	Conversion	Char	Tar	C <sub>1</sub> -C <sub>4</sub> gases
Whole coal	No	46	54	30	7
	Yes	62	38	49	11
Duxin	No	37	63	29	6
	Yes	61	39	45	9
Clarain	No	40	60	27	3
	Yes	54	46	38	9

Fig 1. Tar yields from hydrocracking  
with and without Mo Catalyst.

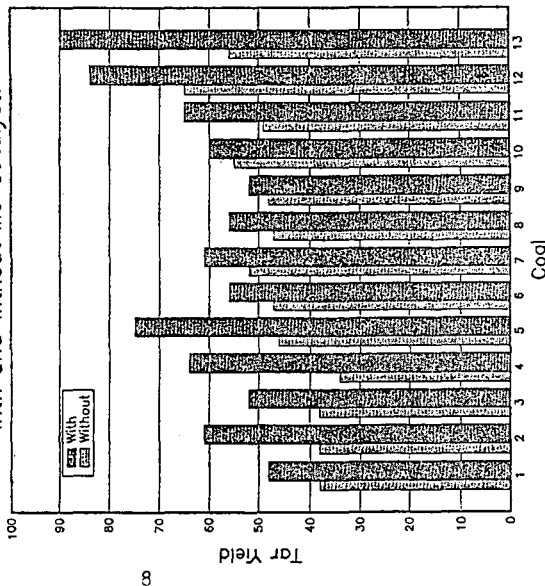


Fig 2. Correlation of total conversion  
without catalyst with volatile  
matter content

